

Dissociation and ionization of small molecules steered by external noise

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(Dated: February 2, 2008)

Abstract

We show that ionization and dissociation can be influenced separately in a molecule with appropriate external noise. Specifically we investigate the hydrogen molecular ion under a stochastic force quantum mechanically beyond the Born-Oppenheimer approximation. We find that up to 30% of dissociation without ionization can be achieved by suitably tuning the forcing parameters.

PACS numbers: 33. 80. Gj, 34. 10. x, 03. 65. Sq

I. INTRODUCTION

The anharmonicity of molecular vibrations makes the dissociation of a molecule by irradiation of laser light a relatively difficult task [1]. Consequently, high intensity is required for dissociation, for instance, $I > 10^{14}\text{W}/\text{cm}^2$ for HF in monochromatic fields [2]. In half cycle pulse fields the situation is improving due to the broad frequency content of this radiation. Even in that case, however, intensities $I > 10^{13}\text{W}/\text{cm}^2$ are required to achieve on the order of 15% dissociation probability [3]. At such high intensities, the ionization process dominates and masks vibrational excitation and dissociation. Chelkowsky et al. [4] suggested that the dissociation threshold of a diatomic molecule can be lowered by two orders of magnitude using a down-chirped laser, tracing the decrease in spacing of the excited energies levels, and hence dissociation without ionization should be possible. In a similar spirit, circularly chirped pulses have been used by Kim et al. [5] for the dissociation of diatomic molecules. They found that the threshold laser intensity is substantially reduced, which may allow to achieve dissociation without ionization.

Recently, dissociation of diatomic molecules under a stochastic force was investigated representing the diatom as a Morse oscillator [6]. A phenomenon, akin to stochastic resonance has also been identified in the interaction of an atom with a strong laser field and additional noise [7].

In the present study, the external force is a sequence of pulses (kicks) at random times, each kick carrying an independent weight [6, 8]. Both, the weights Γ_i and the intervals between kicks Δt_i , follow a Poisson distribution with averages γ and $\langle \Delta t \rangle$, respectively. This type of force, similar to white shot noise, has also been used to model the passage of ions through carbon foils [9]. Through its inherent time-structure characterized by $\langle \Delta t \rangle$, it can couple selectively to bound degrees of freedom with comparable time scales of the noise. Given the difficult dissociation without ionization as described above, it is natural to ask if stochastic forcing may allow one to separate effectively ionization from dissociation.

In order to answer this question we have to include both, nuclear as well as electronic degrees of freedom in our description. The simplest molecule displaying ionization and dissociation is the hydrogen molecular ion H_2^+ in an external field. Using a two-level approximation for the electron [10] or a soft-core potential for the Coulomb interaction [11, 12], this system has been investigated previously under strong laser fields.

As in [13] we refrain from these approximations and investigate this molecule under the influence of a stochastic field with the only restriction that the random force is directed along the molecular axis. This leads to cylindrical symmetry of the problem and therefore 3 degrees of freedom (2 for the electron and one for the nuclei) have to be taken into account explicitly. On the same level, the interaction of H_2^+ with laser light has been investigated recently and a sensitive dependence of the dissociation on the carrier envelope phase has been found [14]. Yet, the maximal dissociation probability reported is below 20 %.

We begin the main text of this paper in section 2 with a description of the noise source and a brief explanation, how quantum evolution under a stochastic force is solved for in time. In section 3 we discuss the influence of the same stochastic force on an atom (electronic degrees of freedom) and a molecule (vibrational degrees of freedom) separately, since the effect of coupling strong noise to quantum systems is not widely known. Then in section 4 we describe how we handle H_2^+ numerically, in particular how we extract ionization and dissociation from the numerically obtained time-dependent wavefunction. In section 5, results for the dissociation and the ionization probability of H_2^+ will be presented and discussed, while section 6 concludes the paper.

II. DESCRIPTION OF THE NOISE SOURCE

The stochastic force $F(t)$ we consider here is given by [8, 15]

$$F(t) = \sum_{i=1}^{N_t} \gamma_i \delta(t - t_i), \quad (1)$$

and stands for a series of random impulses of strength γ_i at times t_i , i. e., $F(t)$ is a kind of white shot noise [16] responsible for multiple δ -kicks undergone by the molecule, where N_t is the number of kicks up to time t controlled by the Poisson counting process N_t . It is characterized by the average kicking interval $\langle \Delta t \rangle \equiv \lambda^{-1}$ about which the actual interval $\Delta t_i = t_i - t_{i-1}$ are exponentially distributed, similarly as the actual kicking strengths γ_i about their mean γ ,

$$P(\Delta t_i) = \lambda \exp(-\lambda \Delta t_i), \quad P(\gamma_i) = \gamma^{-1} \exp(-\gamma_i/\gamma). \quad (2)$$

In analogy to periodically applied half cycle pulses [17], we restrict our analysis to positive γ_i and assume that γ_i and t_i are mutually uncorrelated random variables generated by the

distributions functions of Eq. (2). The determination of $F(t)$ reduces to the construction of a stochastic sequence (γ_i, t_i) which can be done assuming that the random times t_i form a Poisson sequence of points leading to a delta correlated process [8]. It is easy to show [15] that the stochastic force constructed has the properties

$$\begin{aligned}\langle F(t) \rangle &= \gamma\lambda \\ \langle F(t)F(s) \rangle &= 2\gamma^2\lambda\delta(t-s) + \gamma^2\lambda^2,\end{aligned}\tag{3}$$

where $\langle \rangle$ is understood as an average over a sufficient large number of deterministic realizations $j = 1, \dots, N$ of $F(t)$ in terms of specified stochastic sequences $(\gamma_i^{(j)}, t_i^{(j)})$. The corresponding power spectrum, i. e., the Fourier transform of $\langle F(t)F(s) \rangle$, is given by

$$S(\omega) = 4\frac{\gamma^2\lambda}{\sqrt{2\pi}} + \gamma^2\lambda^2\sqrt{2\pi}\delta(\omega).\tag{4}$$

These properties reveal the difference between the present stochastic force (white shot noise) and a pure white noise which is delta-correlated with *zero mean*.

Note that $\langle \Delta t \rangle$ and γ are the two relevant parameters characterizing the present noise source.

The determination of the time evolution of a system with a deterministic Hamiltonian H_0 and an additional stochastic driving $H = H_0 + xF(t)$ is straight forward by solving first the conventional deterministic time-dependent Schrödinger equation for each realization $F^{(j)}$ of the stochastic force, forming from it the desired observable $\mathcal{O}^{(j)}$ and finally averaging over the realizations, $\mathcal{O} = N^{-1} \sum_{j=1}^N \mathcal{O}^{(j)}$.

III. IONIZATION AND DISSOCIATION UNDER STOCHASTIC FORCES

To demonstrate that coupling white shot noise to a bound quantum system is sensitive to the time scale of bound motion, we briefly describe how an atom and a diatomic molecule responds to noise. To this end we show in figure 1 how the electronic ground state of a one dimensional soft-core model of the H-atom and the vibrational ground state of a Morse oscillator describing a HF molecule are depopulated under stochastic forcing. The potential in the atom case is given in atomic units by

$$V(x, t) = V_C + xF_a(t) = -\frac{1}{\sqrt{x^2 + a}} + xF_a(t),\tag{5}$$

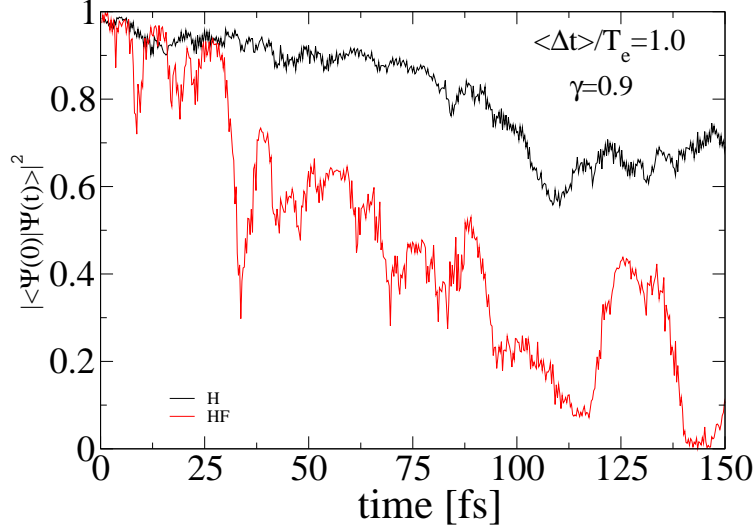


FIG. 1: The population of the (electronic) ground state of the hydrogen H atom versus the population of the vibronic ground state of a Morse oscillator, describing the HF molecule as function of time for the same amount of noise. For HF model, $\mu_0 = 3.54076$ a.u., $\alpha = 1.1741$ a.u., $D = 0.225$ a.u.[19].

with $a = 2$ such that the ground state energy corresponds to that of the 3d hydrogen atom. In the molecular case it is given by

$$V(x) = V_M + \mu_0 x F_m(t) = D(1 - \exp\{-\alpha x\})^2 + \mu_0 x F_m(t) \quad (6)$$

with the dissociation energy D , the length scale α , and the dipole gradient μ_0 . Note that the eigenstates and the eigenenergies of this Morse potential model are exactly known [18]. We expose both systems to the same stochastic external perturbation, as described above, by adjusting the molecular force such that $\mu_0 F_m(t) = F_a(t)$. The average time between kicks is chosen to equal the electronic period in the hydrogen atom, which in atomic units is given by $T_e = 2\pi$.

Numerically, we find a very promising indication that the electron in the atom case does react much less to the force than the binding of the molecule. This is shown in figure 1, where the auto-correlation function of the ground state electron wavefunction for the atomic, as well as of the vibrational ground state in the molecular case is shown. While the atom is still dominantly in its ground state, the ground state of the molecule has already been depopulated by more than 50%.

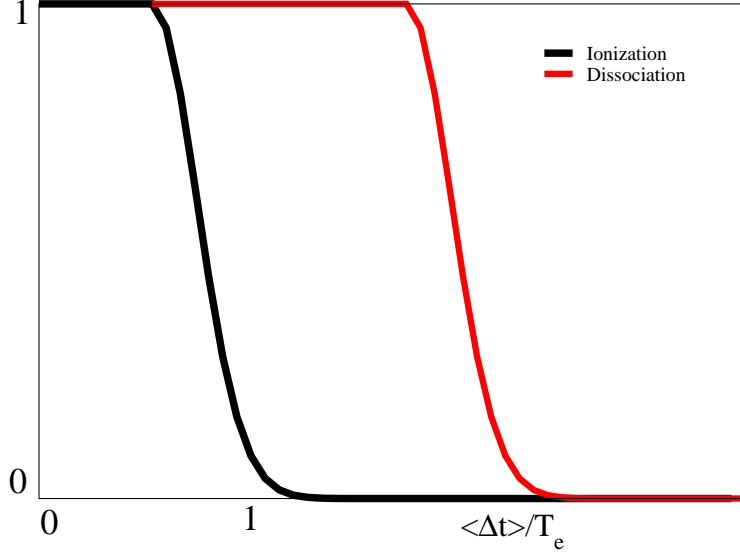


FIG. 2: Schematic ionization and dissociation (including fragmentation) probabilities as function of the kick spacing $\langle \Delta t \rangle / T_e$ at a given finite time and for a given kicking strength γ .

In general, we expect for a system S with a characteristic period T_S^c of bound motion that noise will couple energy into the system if its kick spacing is smaller than the bond period, $\langle \Delta t \rangle < T_S^c$. In the opposite case, $\langle \Delta t \rangle \gg T_S^c$, the bound motion will be insensitive to the noise. Since the molecular vibrational period is much larger than the electronic period in an atom, $T_{\text{vib}}^c \gg T_e^c$, there is a window in $\langle \Delta t \rangle$, where dissociation without substantial ionization should be possible (see the sketch, fig. 2).

We double check this conjecture in the following with the hydrogen molecular ion H_2^+ in an external field which is the simplest molecule displaying both, ionization and dissociation. Since this problem is sensitive to different timescales, we avoid the Born Oppenheimer approximation which could be an (artificial) source of physical effects to be predicted.

IV. MOLECULAR IONIZATION AND DISSOCIATION DYNAMICS IN H_2^+ UNDER EXTERNAL DRIVING

We solve the time-dependent Schrödinger equation for the hydrogen molecular ion in a linearly polarized laser field neglecting the center of mass and the rotational motion [13]. Adding a dipole coupled stochastic force $F(t)$ the time-dependent stochastic Schrödinger

equation is given by (in atomic units)

$$i\frac{\partial}{\partial t}\Psi(z, \rho, R, t) = [K_{\text{vib}} + K_e + V + z\kappa F(t)]\Psi(z, \rho, R, t) \quad (7)$$

with the kinetic energy $K_{\text{vib}} = -M_p^{-1}\partial^2/\partial R^2$ of the protons, the electronic kinetic energy

$$K_e = -\frac{\beta}{2}\frac{\partial^2}{\partial z^2} - \beta\frac{1}{2}\frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho}\frac{\partial}{\partial \rho} \quad (8)$$

and the potential energy

$$V(\rho, z, R) = -[\rho^2 + (z - R/2)^2]^{-1/2} - [\rho^2 + (z + R/2)^2]^{-1/2} + 1/R, \quad (9)$$

where $\beta = 1/2 + 1/(4M_p)$, $\kappa = 1 + 1/(2M_p + 1)$, M_p is the proton mass in units of the electron mass, R is the internuclear distance and z and ρ are cylindrical coordinates of the electron.

Due to the cylindrical symmetry of the stochastically driven system an expansion of the wavefunction in a Bessel-Fourier series in ρ is performed. The singularities of the Coulomb potential is retained, without any softening of the potential. The time-dependent stochastic Schrödinger equation (7) can then be solved by the standard split operator FFT technique [20]. We start from the ground state as initial state $\Psi(\rho, z, R, t = 0)$, represented very accurately by the product of the vibrational ground state $\phi_0(R)$ and the $1s\sigma_g$ electronic wavefunction of H_2^+ .

The observables we are interested in are the ionization probability

$$P_I(t) = 1 - \int_0^{R_{\text{max}}} f_1(R, t) dR \quad (10)$$

and the dissociation probability which is defined *without* ionization according to

$$P_D(t) = \int_{R_D}^{R_{\text{max}}} f_1(R, t) dR. \quad (11)$$

Here, f_1 is obtained by integrating $|\Psi(\rho, z, R, t)|^2$ over electronic coordinates inside a cylinder of radius $\rho_0 = 8$ a.u. and height $2 \times z_I + R$ as sketched in figure 3. The integration area would split into two cylinders if $R > 2z_I$. The splitting, however, is never reached in the present calculation due to the smallness of our R -grid. For $z > z_I + R/2$, the system is considered to be ionized since the electron is sufficiently distant to each of the nuclei. The nuclear separation defining the onset of dissociation into the $H+H^+$ channel is taken as $R_D = 9.5$ a.u. and [13]. In this configuration, f_1 is explicitly given by

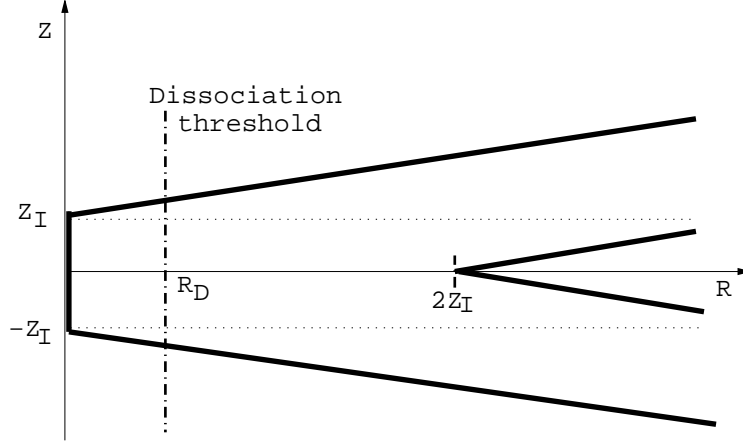


FIG. 3: The region inside the thick solid lines indicates the support of the non-ionized part of the total wavefunction. The vertical dot-dashed line defines the onset of dissociation.

$$f_1(R, t) = 2\pi \int_{-(z_I+R/2)}^{(z_I+R/2)} dz \int_0^{\rho_0} d\rho \rho |\psi(R, z, \rho, t)|^2$$

In our calculations, the electronic grid for z contains 1024 points and extends from -50 a.u. to 50 a.u.. A quadratic imaginary potential has been used to avoid unphysical reflections at the grid boundaries. The onset of ionization was defined to be at $z_I = 32$ a.u.. The nuclear grid consists of 256 points, extending from $R_{\min} = 0.38$ a.u. to $R_{\max} = 24$ a.u. and 16 basis functions were used in the Bessel-Fourier expansion for ρ .

V. NUMERICAL RESULTS

Dissociation and ionization probabilities of H_2^+ as described in the previous section have been obtained for different parameters of the stochastic forcing. Averaging over around 20 realizations of the noise was enough to converge the results for all the cases presented below. The maximum propagation times for the wave function were always well below 500 fs around which which rotational motion of the molecule (not included in the present approach) would come into play.

In figure 4 we present results for a fixed strength $\gamma = 0.9$ a.u. of the noise. The average spacing of the kicks was varied to cover the switching of the dynamics from pure ionization ($\langle \Delta t \rangle / T_e \ll 1$, figure 4a) to pure dissociation ($\langle \Delta t \rangle / T_e \approx 1$, figure 4c). While the ionization

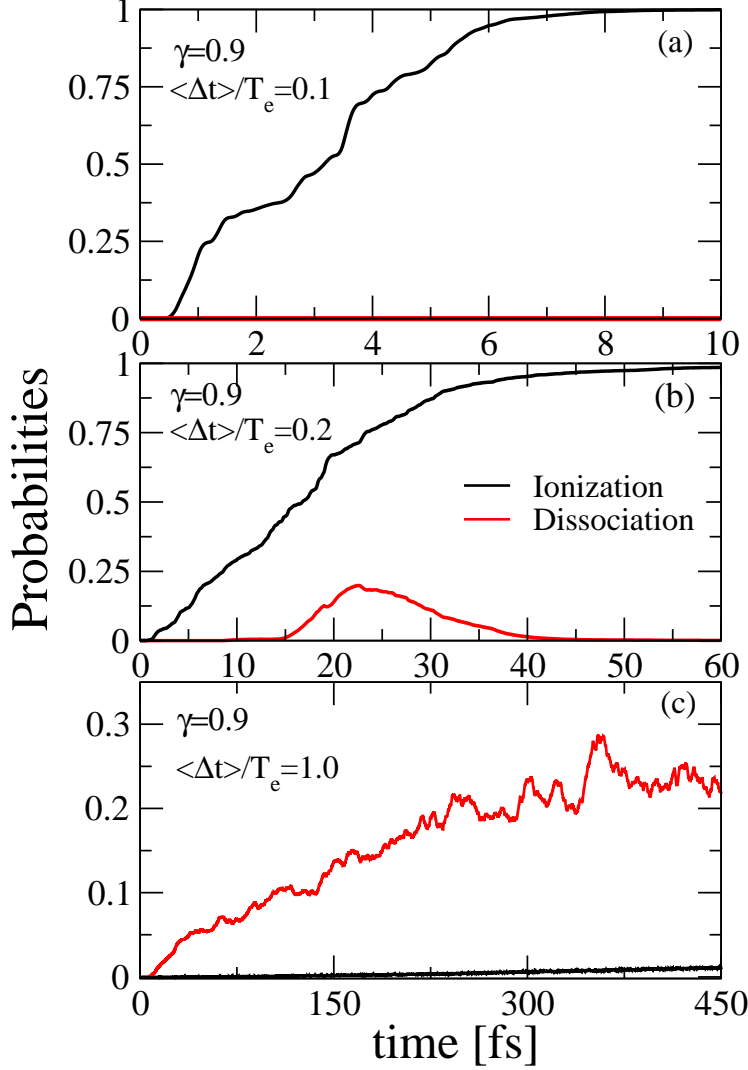


FIG. 4: Ionization and dissociation probabilities as a function of time for different average kick spacings., with $\langle \Delta t \rangle / T_e$ as indicated in panels and for a constant kicking strength $\gamma = 0.9$ a.u.

probability reaches unity the dissociation probability has a maximum of 25 % as can be seen in Figure 4c.

In Figure 5 the spacing between the kicks is fixed at the intermediate value of $\langle \Delta t \rangle / T_e = 0.2$, where both, dissociation and ionization, coexist for a certain amount of time. From a) to c) we reduce the strength of the external forcing. Reducing γ reduces the ionization rate and correspondingly shifts the peak in the dissociation without ionization to later times.

What are close to optimal parameters for dissociation without ionization for the stochastically driven hydrogen molecular ion? This question is answered in figure 6. Here, at

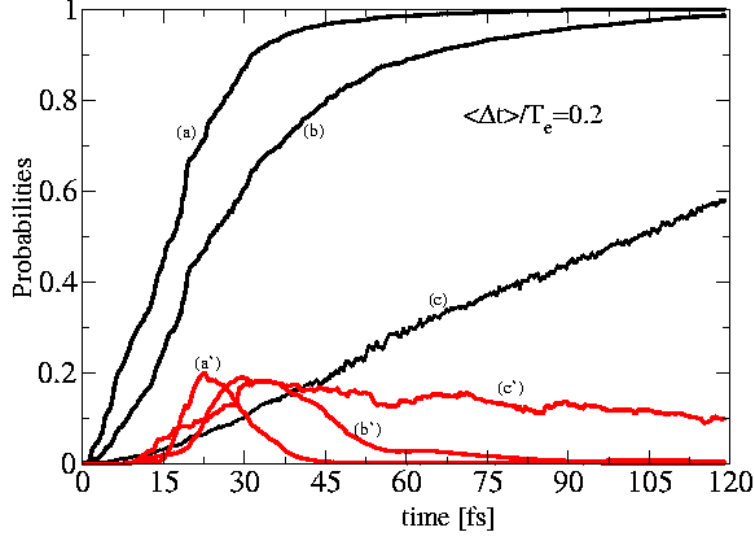


FIG. 5: Ionization (black) and dissociation (red) probabilities as a function of time for different noise strength and for fixed spacing $\langle \Delta t \rangle / T_e = 0.2$: ionization (a) and dissociation (a'): $\gamma = 0.9$ a.u. ionization (b) and dissociation (b'): $\gamma = 0.75$ a.u. ionization (c) and dissociation (c'): $\gamma = 0.5$ a.u.

fixed final time of 100 fs, the probabilities as a function of the average kick intervals are displayed. Beyond $\langle \Delta t \rangle / T_e \approx 1$ the ionization quickly goes to zero. However, also the dissociation approaches zero, as the system does not respond to rare kicks. An intermediate value of $\langle \Delta t \rangle / T_e \approx 0.5$ turns out to maximize dissociation without fragmentation of the whole system. The maximal probability is close to 30 % and therefore higher than any comparable value we have found in the literature. We did many additional calculations for different final times, as well as for different field strengths and found results qualitatively similar to those presented in Figure 6.

These results confirm the expectations from figure 2 with the important difference, that for the real molecule, the onset of ionization limits the maximum dissociation which can be achieved. The actual value of the maximum, of course, can only be calculated as we have done (see figure 6).

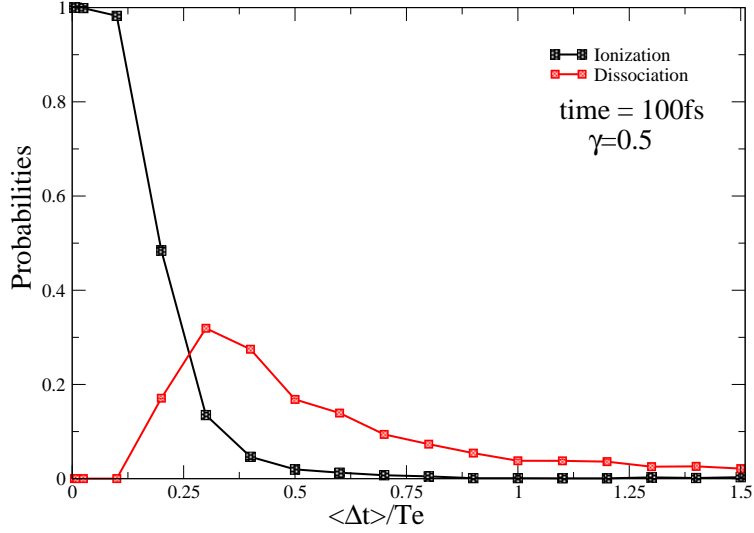


FIG. 6: Ionization and dissociation probabilities as a function of kick spacings at a given finite time for a kicking strength of $\gamma = 0.5$ a.u..

VI. DISCUSSION AND CONCLUSIONS

Achieving efficient dissociation in small molecular systems without ionization has been a longstanding goal. Here, we have explored an alternative to the standard tools, such as chirped laser pulses: the application of stochastic driving in the form of white shot noise with a characteristic internal timescale.

For the hydrogen molecular ion we have shown that dissociation and ionization can be well separated by a suitable choice of the noise parameters. A major role being played by the internal timescale of the noise, the average interval between kicks. At kicking intervals equal to the electronic ground state period of the hydrogen atom the driven system switches between being ionized to dissociating already for moderate field strengths below one atomic unit.

Stochastic driving with the specified properties can be realized with chaotic light, where a short laser pulse with sufficient band width is shaped with random phases and amplitudes of each frequency component [7].

Acknowledgment

Fruitful discussions with Kamal P. Singh and Manfred Lein are gratefully acknowledged. A. K. would like to acknowledge the financial support by the Alexander von Humboldt-Stiftung as well as the Max-Planck-Gesellschaft through a Reimar Lüst grant (2005).

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